Spin-flip Raman scattering of light in a degenerate electron gas in the magnetically mixed crystals $Cd_{1-x}Mn_xS$: In

D. L. Alov, S. I. Gubarev, and V. B. Timofeev

Institute of Solid State Physics, USSR Academy of Sciences

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Exchange interaction with a magnetic impurity leads to giant splitting of the spin states in the degenerate gas of free electrons in $Cd_{1-x}Mn_xS$:In crystals in a magnetic field. This splitting manifests itself in the spectra of Raman scattering with spin flip of the band electrons (spin-flip Raman scattering, SFRS) as an anomalously large value of the spectral shift of the SFRS Stokes component ($\Delta E \approx 7$ meV in a field $H = 50$ kOe; the effective g factor at $T = 1.4$ K and $x \approx 0.015$ is $g^*_e \approx 90$). When the angle θ between the directions of the incident and scattered light changes from zero to 180° the width of the SFRS line changes by more than a decade, from $\Gamma = 0.4$ to 4.5 meV. From the angular dependence of the SFRS line we determined the momentum relaxation time $\tau_k \approx 3 \times 10^{-14}$ sec.

I. INTRODUCTION

Introduction of a magnetic impurity into a semiconductor matrix increases considerably the paramagnetic susceptibility of the free and weakly bound carriers at room temperature.[1,2] The cause of this phenomenon is the presence of strong exchange interaction between the band electrons and the localized d electrons of the paramagnetic impurity. Polarization of the localized magnetic moments of the impurity atoms in an external magnetic field generates a strong exchange field that acts on the carriers in the valence and conduction bands of the semiconductor. The splitting of the spin states in the conduction bands $Cd_{1-x}Mn_xS$ at an Mn molar fraction $x \approx 0.02$ can reach ~ 10 meV, corresponding to an effective electron g factor $g^*_e > 100$. The exchange interaction of the magnetic impurity with holes is even stronger and becomes comparable, at sufficiently high impurity densities, with the value of the spin-orbit and crystalline interaction in the valence band of the semiconductor.[3,4] At the same time, the band parameters of the magnetically mixed semiconductors differ little from the corresponding parameters of the host semiconductor. This affords a unique possibility of investigating in such compounds the electronic properties of semiconductors under conditions of extremely large spin splittings.

Up to now, only compensated samples of magnetically mixed semiconductors have been investigated at a relatively low density of electrically active impurities, $|N_D - N_A| < 10^{17}$ cm^{-3}. What was studied was the influence of the exchange interaction on the energy spectrum of the weakly bound states of the carriers in the semiconductors, such as excitons, exciton-impurity complexes, and neutral donor and acceptor states.[2,5]

We have investigated in the present study exchange interaction in strongly doped crystals of a magnetically mixed semiconductor with donor-impurity density higher than the Mott value ($(N_D - N_A) > 10^{18}$ cm^{-3}). At such densities, the Coulomb interaction in the electron subsystem is screened, and there are no bound states of excitons and shallow neutral donors in the crystal. The electron subsystem itself constitutes at helium temperature a degenerate gas of free electrons, which fills both spin valleys to a common Fermi level with a chemical potential μ (Fig. 1). In a magnetic field, the exchange interaction with the magnetic impurity leads to a splitting ΔE of the spin subbands, giving rise to an appreciable spin polarization of the electron gas.

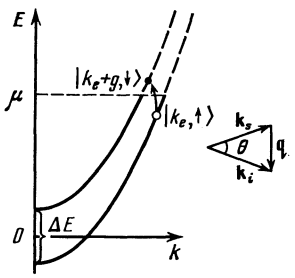

FIG. 1. Scheme of electronic transitions in a degenerate gas in the case of SFRS. μ—chemical potential of the electron gas, ΔE— spin splitting, $\mathbf{k}_i$ and $\mathbf{k}_s$—wave vectors of the incident and scattered light. $\mathbf{q}$—transfer momentum [$q = 2|k_i|\sin(\theta/2)$].

An effective tool for the investigation of spin splittings in semiconductors turned out to be spin-flip Raman scattering of light (SFRS), i.e., inelastic scattering of light, as a result of which the electron goes over from one spin state to another. The SFRS method was successfully used to study a degenerate electron gas in semiconductors without magnetic impurities,[6,7] as well as to study exchange interaction in magnetically mixed semiconductors with low donor-impurity density.[8–11] Since SFRS constitutes scattering by spin-density fluctuations, no collective states of the electron gas are excited in the course of such scattering, which is of the single-particle type. The spin splitting in the electron gas can be directly measured knowing the spectral shift of the SFRS in this case.

The large SFRS spectral shifts observed in magnetically mixed semiconductors permit the investigations to be carried out at appreciable SFRS line widths, and in particular to investigate the Doppler shift of an SFRS line in a wide range of scattering angles. Under conditions when the conduction band is significantly split, electrons located deep below the Fermi surface can take part in the SFRS. This is of interest

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for the study of the spectrum of quasiparticles in a degenerate Fermi gas.

2. EXPERIMENTAL PROCEDURE

The experiments were performed on $Cd_{1-x}Mn_xS$, crystals grown from the melt by the Bridgman method. The molar fraction of Mn in the charge was $x = 0.015$. The donor impurity (In) was added during the crystal growth. The samples had n-type conductivity. The resistivity of the samples at room temperature was $\rho \approx 4.5 \times 10^{-3}\ \Omega \cdot$ cm and depended little on the temperature. The electron density n_e and mobility μ_e at $T = 300$ K were, according to Hall-effect measurements, $n_e \approx 3.5 \times 10^{18}$ cm^{-3} and $\mu_e \approx 300$ cm^2/V · sec.

The samples were parallelepipeds measuring $5 \times 5 \times 3$ mm, with one of the side faces cut at an angle 45° to the C_6 crystal axis. The experiments were performed in a Voigt geometry in magnetic fields up to 60 kOe. The wave vectors of the incident and scattered light were in a plane perpendicular to the magnetic field. The recording was along the crystal hexagonal axis C_6. The angle between the directions of the incident and scattered light was varied from 0 to 180°. The aperture of the collimated beams did not exceed $\approx 2°$.

The excitation with the $\lambda = 5145$ Å in line of an Ar^+ laser. To prevent superheating of the sample the radiation was focused with a cylindrical lens into a strip 3 mm long and 0.5 mm wide, and the excitation power was decreased to 20–40 mW.

The spectral instrument was a DFS-24 double monochromator with linear dispersion 4.5 Å/mm. The scattered light was photoelectrically recorded in the photon-counting regime.

3. EXPERIMENTAL RESULTS AND THEIR DISCUSSION

Only the Stokes component of the SFRS is observed in the investigated crystals. In the case of small-angle scattering ($\theta \approx 0°$) the SFRS spectrum is a relatively narrow line with half-width $\Gamma \approx 0.4$ meV (Fig. 2), whose spectral location and intensity depend on the magnetic field strength. The spectral shift in $Cd_{1-x}Mn_xS$ is anomalously large compared with pure CdS and, depending on the magnetic field, is satu-

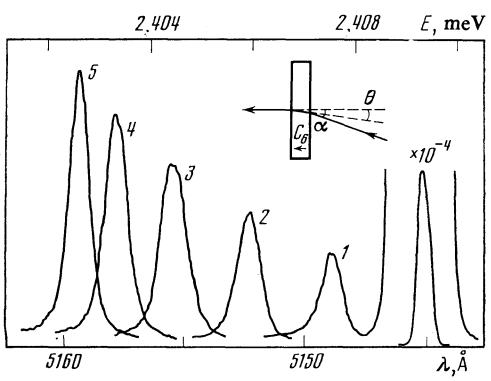

FIG. 2. SFRS spectra in $Cd_{1-x}Mn_xS$: In at $T = 1.4$ K ($x \approx 0.015$, $N_D - N_A = 3.5 \cdot 10^{18}$ cm^{-3} for forward scattering in the following magnetic fields (1 — 3.5; 2 — 7.5; 3 — 12.5; 4 — 21.6; 5 — 36). The inset shows the experimental geometry.

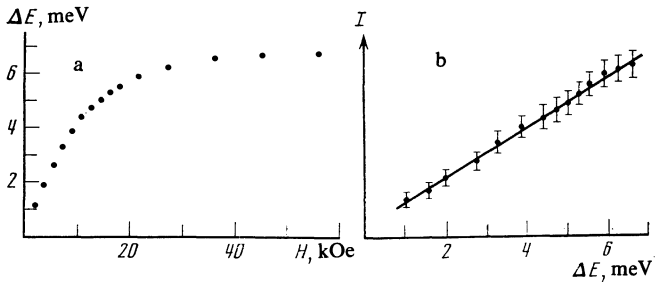

FIG. 3. a) Spectral shift ΔE of SFRS line vs the magnetic field. b) Integrated intensity of SFRS line vs spin splitting ΔE in the conduction band ($T = 1.4$ K, $\theta \approx 3°$).

rable (Fig. 3a). In a field $H = 50$ kOe, the SFRS line is shifted relative to the laser line by an amount $\Delta E \approx 7$ meV. In weak fields, the dependence of the spectral shift on H is linear and can be described by the effective g-factor $g^*_e \approx 90$. In contrast to scattering by the electrons of a shallow neutral donor,[8,9] where the intensity of the SFRS line depended weakly on the magnetic field, in our samples we observed an almost linear dependence of the SFRS intensity on the spectral shift ΔE (Fig. 3b).

The anomalously large spin splitting in the conduction band of $Cd_{1-x}Mn_xS$ in a magnetic field are due to strong exchange interaction between the free-electron spin σ and the magnetic moments of the Mn d electrons. The interactions is usually written in the form[5]

$$H_{ex} = \sum_i J\sigma \mathbf{S}_i \delta(\mathbf{r} - \mathbf{R}_i) |\psi(\mathbf{r})|^2, \tag{1}$$

where J is the exchange integral of the s–d interaction, $\psi(\mathbf{r})$ is the wave function of the free electron, and $\mathbf{S}_i$ is the spin of an Mn atom located at the site $\mathbf{R}_i$.

In the molecular-field approximation, H_{ex} is replaced by its thermodynamic mean value $\langle H_{ex} \rangle$. Averaging over all the random locations of the Mn in the crystal lattice, as well as over the value of the spin localized on the Mn atom, leads to the following expression for the exchange interaction[2,3]:

$$H_{ex} = N_0 x \langle S_{M^z} \rangle_{H,T} J^{uu}. \tag{2}$$

Here N_0 is the number of cation states in 1 cm^3 of the crystal, x is the molar fraction of Mn, $\langle S_{M^z} \rangle_{H,T}$ is the average magnetization of the magnetic-impurity subsystem, J^{uu} is the exchange integral over the unit cell, taken on the periodic part of the Bloch wave function u of the band electron:

$$J^{uu} = \int \langle u | J(\mathbf{r}) \sigma_z | u \rangle \, d\Omega. \tag{3}$$

At $x > 0.01$ the exchange interaction with the magnetic impurity exceeds substantially the direct action of the magnetic field on the electron subsystem, which is made up of Zeeman terms $\mu_B g_e \mathbf{H} \cdot \sigma$ and diamagnetic corrections due to quantization of the orbital motion of the electrons in the magnetic field. The Zeeman terms can be easily taken into account, and the diamagnetic corrections, being small, will be neglected henceforth.

In the case of $Cd_{1-x}Mn_xS$ the conduction band is simple, of s-type with isotropic electron masses. The energy spectrum of the electrons in the magnetic field can be ex-

pressed in this case in the form

$$\varepsilon_{\mathbf{k}}^{\pm}=\hbar^2k^2/2m_e\pm{}^1/_2A, \tag{4}$$

$$A=\mu_B g_e H+\alpha N_0 x\langle S_{M^z}\rangle_{H,T}, \tag{5}$$

where the $\pm$ correspond to the different values of the electron spin, $\alpha=\langle s|J|s\rangle$ is an exchange integral of type (3) on s-type wave functions, g_e is the electron g factor without allowance for the exchange interaction with the magnetic impurity and has a value $g_e\approx 1.8$ for CdS (Ref. 12).

In crystals with not too high a density of Mn ($x\leqslant 0.05$), the average magnetization $\langle S_{M^z}\rangle_{H,T}$ of the magnetic-impurity subsystem is as a rule well parametrized by the expression[13]

$$\langle S_{M^z}\rangle_{H,T}=S_0^* B_{5/2}[\mu_B g_{\mathrm{Mn}} H/(T+T_0)]. \tag{6}$$

Here $B_{5/2}(t)$ is the Brillouin function for spin 5/2, $S^*{}_0$ is the effective angular momentum of the Mn atom and is somewhat smaller than 5/2, since some of the Mn atoms form strongly coupled antiferomagnetic pairs and do not contribute to the magnetization at $H\leqslant 50$ kOe, while T_0 is a constant that describes the antiferomagnetic interaction between the more remote Mn atoms. In our crystals this constant has a value $T_0\approx 0.5$ K. The value of the exchange integral α in the investigated samples is less than that determined in Ref. 9 for $Cd_{1-x}Mn_xS$ from the value $S_0=5/2$.

Under equilibrium conditions, the carriers that make up the electron gas fill both spin subbands and have a chemical potential corresponding to the given carrier density n_e. The distribution functions of the electrons in the various spin valleys can be written in the form

$$f_{\mathbf{k}}^{\pm}=\left(\exp\frac{\varepsilon_{\mathbf{k}}^{\pm}-\mu}{T}+1\right)^{-1}, \qquad \mu\approx\frac{\hbar^2}{2m_e}(3\pi^2 n_e)^{2/3}, \tag{7}$$

where the electron dispersion law $\varepsilon_k^{\pm}$ is given by (4) and (5).

At an electron density $n_e\approx 3.5\times 10^{18}$ cm^{-3}, using the electron effective mass $m_e=0.2m_0$, we obtain for the electron-gas Fermi energy at $H=0$ the value $\varepsilon_F=\mu\approx 38$ meV. The degree of degeneracy of the electron gas at $T\approx 1.4$ K is $\varepsilon_F/T\approx 300$, and the ratio $\varepsilon_F/\Delta E$ satisfies the inequality $\varepsilon_F/\Delta E\geqslant 5$ in the entire range of magnetic fields. In this case the dependence of the electron-gas chemical potential μ on the splitting ΔE can be neglected.

In the SFRS process the electron goes from a state $|\mathbf{k},\uparrow\rangle$ to a state $|\mathbf{k}+\mathbf{q},\downarrow\rangle$, where $\mathbf{q}$ is the transfer momentum. The probability of such a transition is proportional to the product $f_{\mathbf{k}}(1-f_{\mathbf{k}+\mathbf{q}})$, where $f_{\mathbf{k}}$ and $f_{\mathbf{k}+\mathbf{q}}$ are the occupation numbers of the initial and final states. Assuming the SFRS matrix element to be independent of $\mathbf{k}$, we obtain for the integrated SFRS intensity

$$I\propto\int f_{\mathbf{k}}^{+}(1-f_{\mathbf{k}+\mathbf{q}}^{-})\,d^3\mathbf{k}. \tag{8}$$

In the case of forward scattering $\mathbf{q}\approx 0$ and (8) can be approximately written as

$$I\propto\int_0^{\mu+A/2}\frac{\varepsilon^{1/2}\,d\varepsilon}{\exp[(\mu-A/2-\varepsilon)/T]+1}. \tag{9}$$

At splittings larger than T, such that the inequality $\mu\gg\Delta E\gg T$, is satisfied, the SFRS intensity turns out to be proportional to the spin polarization P of the electron system and increases linearly with ΔE, namely,

$$I\propto P=\frac{n_e^{+}-n_e^{-}}{n_e^{+}+n_e^{-}}\approx\frac{3}{4}\frac{\Delta E}{\mu}. \tag{10}$$

The SFRS anti-Stokes component corresponds to electron transitions under the Fermi surface, and in the case of a degenerate electron gas it is substantially weaker than the Stokes component.

Through the Raman scattering the electron subsystem acquires a momentum $\mathbf{q}=\mathbf{k}_i-\mathbf{k}_s$, where $\mathbf{k}_i$ and $\mathbf{k}_s$ are the wave vectors of the incident and scattered photons. If the change of the light frequency in the course of scattering is small, $\Delta\omega\ll\omega_i$, then $|\mathbf{k}_i|=|\mathbf{k}_s|$ and $|\mathbf{q}|=|\mathbf{k}_i-\mathbf{k}_s|=2|\mathbf{k}_i|\sin(\theta/2)$, where θ is the angle between the directions of the incident and scattered light, and $|\mathbf{k}_i|$ is connected with the refractive index n_λ and the light wavelength λ by the relation $\mathbf{k}_i=2\pi n_\lambda/\lambda$.

A characteristic feature of SFRS by free delocalized carriers is the presence of a Doppler shift of the scattered-light frequency. This shift is due to the translational motion of the electrons. The Doppler shift is added to the Zeeman shift due to the splitting of the conduction band in the exchange field [see (4) and (5)]. If the electron moves with velocity $\mathbf{v}$, the SFRS line will be shifted relative to the laser line by an amount $\Delta\omega=\Delta E/\hbar+\mathbf{v}\cdot\mathbf{q}$. In the case of a degenerate gas, at not too large spin splittings, $\Delta E\ll\varepsilon_F$, the main contribution to the SFRS line is made by electrons close to the Fermi surface. The Doppler width of the SFRS line is in this case of the order of $\Delta\omega_D\sim qv_F$. The Fermi velocity in a degenerate gas of electrons at $n_e\sim 10^{18}$ cm^{-3} is of the order of $v_F\sim 10^7$ cm/sec. This leads to Doppler shifts $\Delta\omega_D\sim 10^{12}$ sec^{-1}. However, the time τ_k of momentum relaxation in strongly doped CdS crystal on account of scattering by impurities is $\sim 10^{-13}$–10^{-14} sec, i.e., the condition $\Delta\omega_D\ll 1/\tau_k$ is satisfied. In this case, as shown in Refs. 6 and 7, the Doppler-broadened SFRS line is narrowed by the rapid changes of the electron velocity directions in the gas. Dynamic narrowing leads to a Lorentz profile of the SFRS line, with a full width at half maximum[7]

$$\Gamma=2(\Delta\omega_D)^2\tau_k \tag{11}$$

or after averaging over the Fermi surface

$$\Gamma=2\langle\mathbf{q}\mathbf{v}_F\rangle\tau_k=2Dq^2=2D(4\pi n_\lambda/\lambda)^2\sin^2(\theta/2), \qquad D={}^1/_3 v_F{}^2\tau_k. \tag{12}$$

The SFRS line width is proportional to q^2, in contrast to the purely Doppler broadening, where $\Delta\omega_D\propto q$.

The transfer momentum q can be varied in experiment by changing the angle θ between the directions of the incident and scattered light. With increasing θ the SFRS linewidth increases (Fig. 4a) and changes by more than a decade from $\Gamma=0.4$ meV ($\theta\approx 0°$, $q\approx 0$) to $\Gamma=4.5$ meV ($\theta\approx 180°$, $q\approx 2|k_i|$). The dependence of the SFRS linewidth on $\sin^2(\theta/2)$ is well described by a linear law (Fig. 4b) in accord with Eq. (12). It must be noted that a diffuse width $\Gamma\propto q^2$ is observed up to the maximum momenta $\mathbf{q}\approx 2|k_i|$ at the borderline of the satisfaction of the inequality $\omega_D\ll 1/\tau_k$.

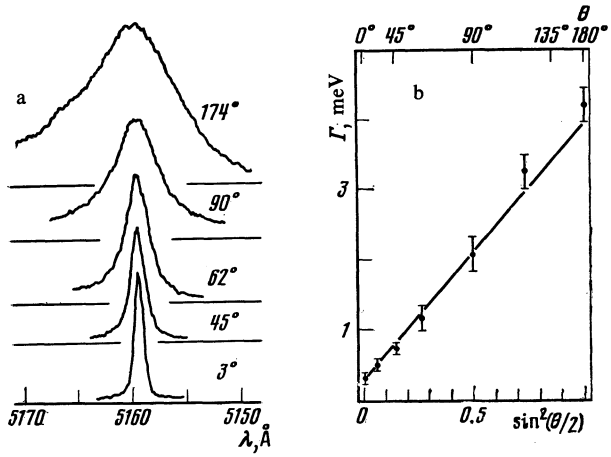

FIG. 4. a) SFRS spectra in $Cd_{1-x}Mn_xS$ at various scattering angles ($T = 1.4$ K, $H = 36$ kOe). b) SFRS linewidth Γ vs the transfer momentum squared $q^2 \propto \sin^2(\theta/2)$.

From the slope of the $\Gamma(q^2)$ line on Fig. 4b we can determine the momentum relaxation time τ_k in the electron gas. Using the value $n_\lambda = 2.5$ at $\lambda = 5145$ Å, we obtain $\tau_k = 3\times 10^{-14}$ sec, which agrees in order of magnitude with the values known[7] for CdS.

The dynamic SFRS-line narrowing observed in experiments with a degenerate electron gas is due to the fact that the SFRS corresponds to transitions with electron spin flip. The spectral shift is connected in this case with the frequency of the electron-spin precession in the exchange field. Electron scattering by impurities is elastic, without spin flip, so that the spin precession of the electron stays in phase. In this respect the case considered differs radically from intra-atomic transitions in a gas of atoms or molecules. In the latter transitions the phase coherence is lost in each collision, so that with increasing collision frequency the spectral width of the line can only increase.

In the case of forward scattering $\mathbf{q} \approx 0$ and there is no Doppler contribution to the SFRS width. In crystals without magnetic impurity the line width is usually related in this case with the times T_1 and T_2 of the longitudinal and transverse electron spin relaxation.[6,7] In magnetically mixed semiconductors, the SFRS line width at $\theta \approx 0°$ is apparently due mainly to exchange-field fluctuations due to the inhomogeneous distribution of the magnetic impurity over the crystal. It is just the exchange-interaction fluctuations which determine the width of the SFRS line by a neutral donor in magnetically mixed semiconductors.[9,10] In the case of a degenerate gas of free electrons, however, the exchange-field fluctuations are considerably weaker. The reason is the delocalized character of the electronic states in the gas, in view of the which the electron undergoes exchange interaction with a considerably larger number of magnetic moments. Thus, if the SFRS line width at $\theta = 0°$ is compared with that observed in $Cd_{1-x}Mn_xS$ ($x = 0.005$; $N_D - N_A = 10^{16}$ cm^{-3}),[9] the SFRS line turns out to be almost three times narrower, even though in our case there is three times more Mn.

The behavior of the SFRS line in weak magnetic fields also differs substantially from that observed in weakly doped crystals. In the case of SFRS by neutral-donor electrons there exists an initial spin splitting of the donor state at $H = 0$, due to formation of a bound magnetic polaron.[9,11] In the case of a degenerate electron gas there is no splitting at $H = 0$, accurate to 0.1 meV. This means that a state of the magnetic polaron type in a degenerate electron gas is greatly weakened compared with the case of weakly bound electrons.

The main features of SFRS by degenerate electrons in magnetically mixed semiconductors can be formulated, as follows: Exchange interaction in an electrons + magnetic impurity system is just as effective at high carrier density as at low density of an electrically active impurity. The SFRS linewidth for forward scattering is much narrower than in the case of scattering by bound electrons of a neutral donor. The intensity of the SFRS line increases linearly with increasing spin splitting, the SFRS linewidth depends on the geometry of the experiment and increases with increasing angle between the incident and scattered light, and a quadratic dependence of the linewidth on the transfer momentum q is observed here.

In conclusion, the authors thank M. P. Kulakov for growing the $Cd_{1-x}Mn_xS$: In crystals with specified densities of the magnetic (Mn and electrically active (In) impurities.

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